

## Synthesis, Spectral and Antibacterial Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Acetone Acetyl hydrazone

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### ABSTRACT

Hydrazone complexes of Co(II), Ni(II), Cu(II) and Zn(II) with acetone acetylhydrazone(AAH) ligand derived from the condensation of acetone and acetylhydrazine, containing N and O donor sites have been synthesized. The complexes are characterized by different physicochemical methods, elemental analysis, molar conductivity, IR, UV-Vis spectra and also magnetic measurements. The discussion of the out come data of the prepared complexes indicate that AAH behave as a neutral bidentate ligand. The electronic spectra as well as their magnetic moments suggest octahedral geometry for the bis- and tris- complexes,  $[M(AAH)_2Cl_2]$ ,  $[M(AAH)_3](NO_3)_2$   $[M= Co(II), Ni(II), Cu(II), Zn(II)]$  and the mixed ligand complex  $[Ni(AAH)(Py)_2Cl_2]$  and tetrahedral geometry for the mono complexes  $[M(AAH)Cl_2]$   $[M= Co(II), Cu(II), Zn(II)]$  and the other prepared mixed ligand complexes  $[Co(AAH)(Py)_2]Cl_2$  and  $[Cu(AAH)(Py)Cl]Cl$ . The antimicrobial properties of the ligand and most of its complexes were studied using Gram-positive and Gram-negative bacteria. The metal complexes were found to have a moderate activity and Zn(II) complexes were the most active.

**Keywords:** Hydrazone, Complexes, Cobalt(II), Nickel(II), Copper(II), Zinc(II).

(II) (II) (II) (II)

.(II) (II) (II) (II)

(IR, UV-Vis.)

$[M(AAH)_2Cl_2]$ ,

$[Ni(AAH)(Py)_2Cl_2]$

(M= Co(II), Ni(II), Cu(II), Zn(II))

$[M(AAH)_3](NO_3)_2$

$[M= Co(II), Cu(II), Zn(II)]$

$[M(AAH)Cl_2]$

$[Cu(AAH)(Py)Cl]Cl$   $[Co(AAH)(Py)_2]Cl_2$

.(II) (II) (II) (II)

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## INTRODUCTION

Hydrazones are promising ligands from the view point of coordination chemistry because of their ability towards complexation with transition and non-transition metals (Raveendran and Pal, 2009; Galic *et al.*, 2011; Matoga *et al.*, 2012), and the wide range of biological and non-biological properties (Matoga *et al.*, 2011; Suvarapu *et al.*, 2012; Mackova *et al.*, 2012). Among the ligand systems, hydrazones occupy a special place because many transition metal complexes of these ligands have been developed due to their chelating capabilities, structural flexibility, interesting electrical as well as magnetic properties (Rao *et al.*, 1997; Vinuelas-Zahinos *et al.*, 2009; Galic *et al.*, 2011; Sadhukhan *et al.*, 2011; Matoga *et al.*, 2012; Datta *et al.*, 2012). Due to short N-N bond length, the hydrazone ligands act mostly as bidentate (NO) moieties although they have the potential to act as tridentate ligands (ONN) in ligand systems containing groups having other donor sites (e.g., Heterocyclic rings) (Jang *et al.*, 2005).

It is well established that the formation of metal complexes plays an important role to enhance the biological activity of free hydrazones (Suvarapu *et al.*, 2012; Mackova *et al.*, 2012). Therefore, the chemistry of transition metals with hydrazones has been of interest to coordination as well as bio-inorganic chemists. In an analytical chemistry also, hydrazone ligands find wide applications as transition metal binders (Suvarapu *et al.*, 2012).

Acetone hydrazones of various aromatic carboxylic acid hydrazides were prepared and their complexes with some transition metal ions have been studied. They show versatile binding modes and applications (Aggarwal, and Rao, 1978; Chowdhury *et al.*, 2008; Ibrahim *et al.*, 2009; Matoga *et al.*, 2011; Matoga *et al.*, 2012). Recently, acetone hydrazone of 3-hydroxy-2-naphthoyl hydrazide form a number of novel compounds with Cu(II), Co(II) and Ni(II) having polymeric structures and affording conducting metallopolymeric films upon electropolymerization (Matoga, 2013).

On the other hand, coordination compounds of aromatic hydrazones have been thoroughly investigated, in contrast, metal complexes based on aliphatic hydrazones (Vinuelas-Zahinos *et al.*, 2009; Sadhukhan *et al.*, 2011; Datta *et al.*, 2012) are yet to be explored. Herein we report a number of acetone acetylhydrazone complexes with various transition metal salts. The present paper describes the syntheses and characterization of these complexes by various physico-chemical techniques and testing of the antibacterial activity of some of them.

## EXPERIMENTAL

### I- Material and Methods

All chemicals used were reagent grade from Fluka or B.D.H. companies, used as supplied. The metal content of the complexes was determined volumetrically (Ni, Cu, Zn) against standard EDTA using suitable indicator (Vogel, 1989). Cobalt was determined spectrophotometrically (Marczenko and Balcerzak, 2000) chloride content was estimated by Mohr's method (Vogel, 1989). The IR spectra of the ligand and its complexes were recorded as KBr pellets in the region 4000-400  $\text{cm}^{-1}$  on Tensor 27 Brucker FT-IR spectrophotometer. Conductivity measurement was performed on  $10^{-3}$  M solutions of the complexes in DMF and /or acetonitrile at room temperature (Ca. 25°C), using PMC3 Jeneway and Terminal 740 wtw conductivity meters. Electronic spectra were recorded on Shimadzu UV – 1650 PC spectrophotometer for  $10^{-3}$  M solutions of the ligand and complexes in DMF or acetonitrile solvents at room temperature. Magnetic susceptibility measurements of the complexes were carried out using Bruker BM6 instrument at ambient temperature. Melting points were determined using electrothermal 9300 apparatus.

## II. Preparation of ligand

### II. a- Preparation of Acetylhydrazine

It was prepared by the reaction of ethylacetate and hydrazine hydrate as described previously (Alsaady and Al-Daher, 2000) and purified by recrystallization from chloroform/ ether mixture. The white crystalline solid obtained is hygroscopic stored in dry conditions mp. 62 °C (Ahmed and Chaudri, 1971).

### II. b- Preparation of acetone acetyl hydrazone (AAH)

Acetylhydrazine (3.7 g, 0.05 mole) was dissolved in dry acetone (20 mL) with continuous stirring, exothermic reaction takes place. The stirring continued for further 30 minutes and the solution obtained was allowed to stand overnight upon which white crystalline solid formed. The solid was then separated by decantation washed with cold acetone (5 mL) dried by vacuum and kept in a desiccator over anhydrous  $\text{CaCl}_2$ . Yield 85% m.p. 96 °C (Chowdhury *et al.*, 2008).

## III. Preparation of metal complexes:

### III. a- Preparation of the bis-complexes [ $\text{M}(\text{AAH})_2\text{Cl}_2$ ] M= Co(II), Ni(II), Cu(II), Zn(II).

Acetone acetylhydrazone (AAH) (0.228 g, 2 mmol) in absolute ethanol (10 mL) was gradually added to (10 mL) ethanolic solution of metal chlorides (1 mmol) [ 0.238 g,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.238 g,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.171 g,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.136 g,  $\text{ZnCl}_2$ ] with continuous stirring. After a complete addition the solution was heated under reflux for 1 h then left to stand over night upon which crystalline solid formed. The solid was then separated, washed with cold ethanol ( $2 \times 2$  mL) followed by ether (5 mL) and dried in an oven at 70 – 80° C.

### III. b- Preparation of mono complexes [ $\text{M}(\text{AAH})\text{Cl}_2$ ], M= Co(II), Cu(II), Zn(II).

These were prepared as described in (IIIa) above except that 1:1 (metal ; ligand) molar ratio were used and an oily residue was obtained on addition of ether (10 mL) to the cold reaction mixture, which redissolved in acetone (10 mL) and left to crystallize out. The solid was then separated and washed with ether (5 mL) and dried as above.

### III. c- Preparation of tris-complexes [ $\text{M}(\text{AAH})_3(\text{NO}_3)_2$ ], M= Co(II), Ni(II), Cu(II), Zn(II).

These complexes were prepared as described in (III-a) above except that (1:3) (metal: ligand) molar ratio were used, (0.342 g, 3 mmol) AAH and (1 mmol) metal nitrate hydrate (0.291 g,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 0.291 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 0.242 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ; 0.297 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). The complexes were separated, washed and dried as in (IIIa) above.

### III. d- Preparation of the mixed ligand complexes :

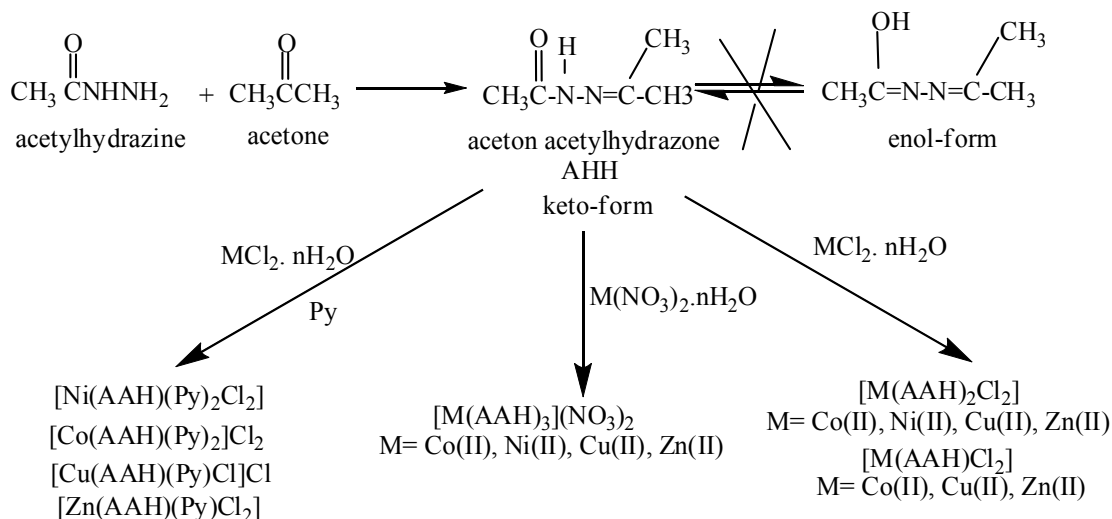
The ligand AAH (0.228 g, 2 mmol) dissolved in pyridine (5 mL) was added to an ethanolic solution (10 mL) of metal chloride (1 mmol). The reaction mixture was then stirred at room temperature for 3h. The volume of the reaction mixture was reduced to ca. 5 mL and ether (10mL) was added upon which oily residue was separated. The oil was redissolved in (5 mL) ethanol and ether was added to cloudiness and left in an ice bath overnight to obtain coloured solids separated by decantation, washed with ether ( $3 \times 3$  mL) and finally dried as above.

## Antibacterial activity

The antibacterial activity of the ligand and some of its complexes were studied using agar diffusion method (Kethcum, 1988). Gram positive bacteria *Staphylococcus aureus* and Gram negative bacteria *Escherichia coli* were cultivated in nutrient agar on petridishes. The test solution was prepared by weighing (10 mg) of all tested substance then dissolved in (1 mL) DMSO. A 6 mm diameter filter paper discs were soaked in the tested solutions. After 24 h cultivation at 37 °C, diameters of zones of inhibition were determined. DMSO was inactive under applied conditions.

## RESULTS AND DISCUSSION

Acetone acetylhydrazone (AAH) was prepared in high yield by condensation reaction of acetylhydrazine and acetone Scheme 1. Exothermic reaction takes place by dissolving acetylhydrazine in an excess of acetone at room temperature. The produced hydrazone separated as stable white crystalline and non – hygroscopic solid unlike the starting material (acetylhydrazine) which is extremely hygroscopic.



**Scheme 1**

Acetone acetylhydrazone react with hydrated metal chloride in 1:2 (metal : ligand) molar ratio in ethanol to produce bis complexes  $[\text{M}(\text{AAH})_2\text{Cl}_2]$  [ $\text{M} = \text{Co(II), Ni(II), Cu(II), Zn(II)}$ ] and in 1:1 molar ratio gave the mono-complexes  $[\text{M}(\text{AAH})\text{Cl}_2]$  [ $\text{M} = \text{Co(II), Cu(II), Zn(II)}$ ] except in case of Ni(II) the bis-complexes  $[\text{Ni}(\text{AAH})_2\text{Cl}_2]$  obtained in both cases. All chlorocomplexes (1-7) Table 1, are non-electrolytes as indicated by their molar conductance in DMF and in MeCN at room temperature. The values of molar conductance for mono-complexes (5-7) in DMF are higher than that expected for non-electrolyte complexes may be due to the displacement of some of the coordinated chloride ions in coordination sphere by strong coordinating solvent DMF while in methyl cyanide (MeCN) the molar conductance measurement are within the range of non-electrolyte complexes (Geary, 1971).

The reaction of the ligand AAH with metal nitrates gave the tris-complexes  $[\text{M}(\text{AAH})_3](\text{NO}_3)_2$  [ $\text{M} = \text{Co(II), Ni(II), Cu(II), Zn(II)}$ ]. The molar conductance data (Table 1), indicated that these are 1:2 electrolyte (Geary, 1971).

Many unsuccessful attempts have been made to isolate complexes of acetone acetylhydrazone in the deprotonated enol form similar to these reported for aromatic hydrazones (Singh *et al.*, 1984; Zhao *et al.*, 2012; Shit *et al.*, 2009) by carrying out the reaction in basic medium in presence of acetate, triethylamine or pyridine. Instead, the later case gave mixed ligand hydrazone, pyridine complexes (12-15). Molar conductance measurements (Table 1), showed that Ni(II) and Zn(II) complexes (12, 15) are non-electrolytes and Co(II) complex (13) is 1:2 electrolyte while Cu(II) complex (14) is 1:1 electrolyte both in DMF and MeCN solutions.

All the complexes are quite stable in air non-hygroscopic soluble in polar solvents, insoluble in ether and having defined melting points suggesting non-polymeric nature of the complexes. The chemical analyses and physical properties of the ligand and its complexes are given in Table 1.

**Table 1: Analytical data and physical properties of the AAH complexes.**

| No. | Complex  | Colour       | M.P.<br>° C | % Yield | % M<br>Found(Calcd.) | % Cl<br>Found(Calcd.) | Ohm <sup>-1</sup> .cm <sup>2</sup> .mole <sup>-1</sup> |       |
|-----|--|--------------|-------------|---------|----------------------|-----------------------|--|-------|
|     |  |              |             |         |                      |                       | DMF  | MeCN  |
| L   | AAH  | White        | 96          |         |                      |                       |  |       |
| 1   | [Ni(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | Bluish-green | 224-226     | 65.8    | 16.26(16.41)         | 20.69(19.84)          | 14.1   | 18    |
| 2   | [Co(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | Pink         | 246-248     | 62.5    | 15.76(16.46)         | 19.52(19.83)          | 20.4   | 22    |
| 3   | [Cu(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | Dark-green   | 172         | 67.3    | 18.39(17.52)         | 19.33(19.58)          | 6.3  | 12    |
| 4   | [Zn(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | White        | 244         | 69.2    | 17.35(17.94)         | 20.39(19.48)          | 29.1   | 25    |
| 5   | [Co(AAH)Cl <sub>2</sub> ]                              | Blue         | 118         | 68.6    | 24.15(24.25)         | 28.71(29.11)          | 51.1   | 17.8  |
| 6   | [Cu(AAH)Cl <sub>2</sub> ]                              | Pale-green   | 172-174     | 72.3    | 26.42(25.56)         | 29.51(28.56)          | 75.1   | 26.9  |
| 7   | [Zn(AAH)Cl <sub>2</sub> ]                              | White        | 258         | 63.7    | 26.21(26.11)         | 27.98(28.35)          | 39.9   | 26.0  |
| 8   | [Ni(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | Pale blue    | 244         | 64.4    | 11.93(11.19)         |                       | 123.5  | 205   |
| 9   | [Co(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | Pink         | 136         | 67.7    | 10.97(11.22)         |                       | 84.5   | 164   |
| 10  | [Cu(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | Dark-green   | 96          | 69.5    | 12.54(12.00)         |                       | 135.3  | 151   |
| 11  | [Zn(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | White        | 142-144     | 68.8    | 13.10(12.30)         |                       | 97.5   | 203   |
| 12  | [Ni(AAH)(Py) <sub>2</sub> Cl <sub>2</sub> ]            | Bluish-green | 308         | 63.5    | 15.34(14.62)         | 18.24(17.67)          | 30.5   | 27.5  |
| 13  | [Co(AAH)(Py) <sub>2</sub> Cl <sub>2</sub> ]            | Blue         | 198         | 62.5    | 13.70(14.66)         | 17.88(17.66)          | 143.1  | 167.2 |
| 14  | [Cu(AAH)(Py)Cl]Cl                                      | Blue         | 226         | 64.1    | 18.71(19.40)         | 21.81(21.67)          | 62.3   | 64.7  |
| 15  | [Zn(AAH)(Py)Cl <sub>2</sub> ]                          | White        | 196         | 63.4    | 20.73(19.85)         | 22.11(21.55)          | 24.7   | 26.3  |

### Infrared Spectra

The significant IR bands of acetone acetylhydrazone (AAH) and its complexes along with their tentative assignments are reported in (Table 2) used for the establishment of the mode of the coordination of hydrazone ligand towards the metal ion. The IR spectrum of acetone acetylhydrazone displays bands at (3238 and 3209) assigned for  $\nu_{\text{NH}}$ , and 1668, 1622 and 982 assignable to  $\nu_{\text{C=O}}$ ,  $\nu_{\text{C=N}}$  and  $\nu_{\text{N-N}}$  stretching frequencies respectively.

The presence of the bands due to amide  $\nu_{\text{NH}}$  and  $\nu_{\text{C=O}}$  stretching frequencies in the spectra of all prepared complexes indicating the coordination of AAH in the keto-form. The  $\nu_{\text{NH}}$  stretching frequency is almost unchanged or shifted to higher frequencies indicating the non-involvement of this group in coordination and a decrease in hydrogen bonding in complex formation may occur. On the other hand, a considerable negative shift in  $\nu_{\text{C=O}}$  band was observed indicating a decrease in the stretching force constant of (C=O) band as a consequence of coordination through the carbonyl oxygen atom of the ligand (Liang *et al.*, 2010; Zaho *et al.*, 2012).

On the other hand, the value of  $\nu$  (C=N) stretching vibration is found to be lower (8-52 cm<sup>-1</sup>) than the  $\nu_{\text{C=N}}$  of the free ligand, (Table 2). This lower value of  $\nu$  (C=N) stretching may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom (Chowdhury *et al.*, 2008). The positive shift of (15-36 cm<sup>-1</sup>) in the  $\nu_{\text{N-N}}$  stretching mode is another evidence for coordination of azomethine nitrogen atom which decreases the repulsion between the lone pair of electrons on the adjacent nitrogen atoms (Shit *et al.*, 2009).

The ligand coordination is substantiated by new bands appearing at (577- 625 cm<sup>-1</sup>) and (507- 540 cm<sup>-1</sup>) in the spectra of the complexes, these are mainly attributed to  $\nu$  (M-O) and  $\nu$  (M-N) respectively.

The metal nitrate complexes (8-11) exhibit a very strong band at the region 1381- 1387 cm<sup>-1</sup> and a medium intensity band at the region 823-825 cm<sup>-1</sup>, which are attributed to the  $\nu_3$ ,  $\nu_2$  vibrations, respectively of uncoordinated nitrate ion of D<sub>3h</sub> symmetry which is in a good agreement with the molar conductance data in (Table 1). (Nakamoto, 1986; Liang *et al.*, 2010)

Pyridine containing complexes (12-15) show two characteristic bands at 702-760 cm<sup>-1</sup> and 630-640 cm<sup>-1</sup> assignable to in-plane and out of plane deformation frequencies of coordinated pyridine molecules (Nakamoto, 1986).

**Table 2: Some selected frequencies (cm<sup>-1</sup>) of the ligand and its complexes**

| Comp. No. | $\nu$ (NH)      | $\nu$ (C=O) | $\nu$ (C=N) | $\nu$ (N-N) | $\nu$ (M-O) | $\nu$ (M-N) | $\delta$ py  | $\nu$ (NO <sub>3</sub> ) |
|-----------|-----------------|-------------|-------------|-------------|-------------|-------------|--------------|--------------------------|
| L         | 3238m<br>3209m  | 1668s       | 1622s       | 982m        |             |             |              |                          |
| 1         | 3195m<br>3153m  | 1635s       | 1589s       | 1007m       | 606m        | 515w        |              |                          |
| 2         | 3188s           | 1653s       | 1589s       | 1007w       | 607m        | 537m        |              |                          |
| 3         | 3219s<br>3157m  | 1635s       | 1576s       | 1012w       | 600w        | 526m        |              |                          |
| 4         | 3246s           | 1655s       | 1585s       | 1014m       | 619m        | 511m        |              |                          |
| 5         | 3261s<br>3172m  | 1651s       | 1597s       | 1007w       | 619m        | 511m        |              |                          |
| 6         | 3238s<br>3178s  | 1653s       | 1614s       | 1012w       | 621m        | 540w        |              |                          |
| 7         | 3230<br>3170    | 1637s       | 1570s       | 1001w       | 625w        | 513m        |              |                          |
| 8         | 3253s           | 1653s       | 1589m       | 1005w       | 606m        | 526w        |              | 1383s<br>825s            |
| 9         | 3276s<br>3184s  | 1647s       | 1587s       | 999w        | 598m        | 523m        |              | 1381s<br>824s            |
| 10        | 3224<br>3161    | 1640s       | 1597s       | 1018w       | 609m        | 526w        |              | 1385s<br>824s            |
| 11        | 3238m<br>3175m  | 1635s       | 1570m       | 997m        | 590m        | 519w        |              | 1387s<br>823s            |
| 12        | 3255 s<br>3138m | 1653s       | 1604s       | 1011m       | 592m        | 515w        | 702s<br>630m |                          |
| 13        | 3265s<br>3197m  | 1654s       | 1614s       | 1016m       | 596m        | 507w        | 758s<br>630m |                          |
| 14        | 3275m           | 1655s       | 1606s       | 1018m       | 577m        | 507w        | 760s<br>652m |                          |
| 15        | 3252m           | 1645s       | 1608s       | 1016m       | 582m        | 517w        | 726s<br>640m |                          |

### Electronic Spectra and Magnetic Properties

The nature of the ligand field around the metal ion and the geometry of the metal complexes have been deduced from the electronic spectra of the metal complexes.

The spectrum of the ligand shows two high and medium intensity bands at 36232 and 30769 cm<sup>-1</sup> due to  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions of the carbonyl and azomethine groups of the ligand. These were shifted to high or lower frequencies Table 3 indicating a coordination of the ligand though the donor atoms of its functional groups( Galic *et al.*, 2011)

In case of Ni(II) complexes (1, 8, 12) three bands at 25445-26525 cm<sup>-1</sup>, 14790-16393 cm<sup>-1</sup> and 9433-10890 cm<sup>-1</sup> are observed due to  $^3A_{2g} \rightarrow ^3T_{1g}(p)$ ,  $^3A_{2g} \rightarrow ^3T_{1g}(F)$  and  $^3A_{2g} \rightarrow ^3T_{2g}(F)$  transitions, respectively, suggesting an octahedral geometry around the Ni(II) ion (Kumar and Radhakrishnan, 2011). The magnetic moment values of Ni(II) complexes are in the range (3.19-3.22) BM which is slightly higher than the spin only (2.83) BM value and indicates an octahedral environment around Ni(II) ions Table 3. The electronic spectrum of cobalt (II) complexes (2, 9) exhibits bands at the ranges 16501- 19011 cm<sup>-1</sup>, 11757-14881 cm<sup>-1</sup> and 9700-9818 can be assigned to  $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ ,  $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$  and  $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ , transition respectively for octahedral Co(II) complexes. The magnetic moment values of (4.90 and 4.72) B.M. of these two

complexes supports the presence of an octahedral geometry around Co(II) (Singh *et al.*, 2013). The other two Co(II) complexes (5, 13) have lower values of magnetic moments (3.85- 3.80 BM) and have intense bands at 14619 and 15105  $\text{cm}^{-1}$  respectively assignable to  ${}^4T_1 \longrightarrow {}^4T_{1(P)}$  transition characteristic for tetrahedral Co(II) complexes.

The green coloured Cu(II) complexes (3, 10) exhibit a single broad a symmetric band in the region 13123-13157  $\text{cm}^{-1}$ . The broadness of the band indicates the three transitions  ${}^2B_{1g} \longrightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \longrightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \longrightarrow {}^2E_g$  which are close in energy. The broadness of the band may be due to Jahn-Teller distortion. The magnetic values of the two complexes (3, 10) are 2.01 and 2.09 BM respectively slightly higher than spin only value for one unpaired electron. All of these data suggests a distorted octahedral geometry around the Cu(II) ion. On the other hand the spectra of Cu(II) complexes (6, 14) in methylcyanide ( $10^{-3}$  M) solution show two d-d transition bands in the region 11210-11415 and 21645-22123  $\text{cm}^{-1}$  which are in close agreement with those expected for a pseudo tetrahedral structure (Lever, 1984). The magnetic susceptibility measurement of these complexes are observed in the range (1.76-1.89) B.M. which confirm the proposed distorted tetrahedral structure (Betanzos- Lara *et al.*, 2013).

In the spectra of diamagnetic zinc(II) complexes (4, 7, 11, 15), as expected, there were only the bands characterizing the ligand displaced to other values compared with the corresponding bands in the spectrum of the free ligand, which proves the coordination of the ligand to the metal ion.

**Table 3: Magnetic susceptibility and electronic spectra of the ligand and its complexes**

| Complex No. | $\mu_{\text{eff}}$ BM | Electronic spectra                      | Solvent |
|-------------|-----------------------|---|---------|
| <b>L</b>    | -                     | 36232, 30769                            |         |
| <b>1</b>    | 3.22                  | 36765, 26525, 14790, 10890              | DMF     |
| <b>2</b>    | 4.90                  | 37037, 28735, 16501, 14881, 9700        | DMF     |
| <b>3</b>    | 2.01                  | 36764, 34013, 13123                     | DMF     |
| <b>4</b>    | Dia                   | 36496, 31645                            | DMF     |
| <b>5</b>    | 3.85                  | 41322, 35971, 14619                     | MeCN    |
| <b>6</b>    | 1.89                  | 40983, 28409, 21645, 11415              | MeCN    |
| <b>7</b>    | Dia                   | 45871, 4006                             | MeCN    |
| <b>8</b>    | 3.22                  | 36764, 32258, 25445, 16393, 10162       | DMF     |
| <b>9</b>    | 4.72                  | 36231, 29239, 19011, 11757, 9818        | DMF     |
| <b>10</b>   | 2.09                  | 34246, 27397, 13157                     | DMF     |
| <b>11</b>   | Dia                   | 37037, 29069                            | DMF     |
| <b>12</b>   | 3.19                  | 38461, 35087, 28735, 25575, 15432, 9433 | DMF     |
| <b>13</b>   | 3.80                  | 35971, 30864, 15105                     | DMF     |
| <b>14</b>   | 1.76                  | 40000, 33112, 22123, 11210              | MeCN    |
| <b>15</b>   | dia                   | 36764, 32258                            | DMF     |

### Antibacterial activity

The antibacterial activity of the newly synthesized hydrazone (AAH) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes against Gram positive *Staph. aureus* and Gram negative *E. coli* organism have been studied by the disk diffusion method (Collee *et al.*, 1989). The antibacterial results suggest that the complexes (Table 4) shows a moderate activity against both types of bacteria. They show higher antibacterial activity than the ligand, specially Zn(II) complexes which show the highest activity. The solvent DMSO was inactive against any bacterial strain.

**Table 4: Antibacterial activity of the ligand and its complexes**

| Comp. No. | Empirical formula                                      | <i>Staph. aureus</i>             | <i>E. coli</i>                   |
|-----------|--|----------------------------------|----------------------------------|
|           |  | Diameter of inhibition zone (mm) | Diameter of inhibition zone (mm) |
| <b>L</b>  | C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O        | 6                                | 6                                |
| <b>1</b>  | [Ni(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | 7                                | 6                                |
| <b>2</b>  | [Co(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | 9                                | 10                               |
| <b>3</b>  | [Cu(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | 10                               | 7                                |
| <b>4</b>  | [Zn(AAH) <sub>2</sub> Cl <sub>2</sub> ]                | 12                               | 9                                |
| <b>8</b>  | [Ni(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | 6                                | 6                                |
| <b>9</b>  | [Co(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | 9                                | 9                                |
| <b>10</b> | [Cu(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | 9                                | 8                                |
| <b>11</b> | [Zn(AAH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> | 10                               | 7                                |
| <b>12</b> | [Ni(AAH)(Py) <sub>2</sub> Cl <sub>2</sub> ]            | 7                                | 6                                |
| <b>13</b> | [Co(AAH)(Py) <sub>2</sub> Cl <sub>2</sub> ]            | 10                               | 10                               |
| <b>14</b> | [Cu(AAH)(Py)Cl]Cl                                      | 9                                | 9                                |
| <b>15</b> | [Zn(AAH)(Py)Cl <sub>2</sub> ]                          | 17                               | 10                               |

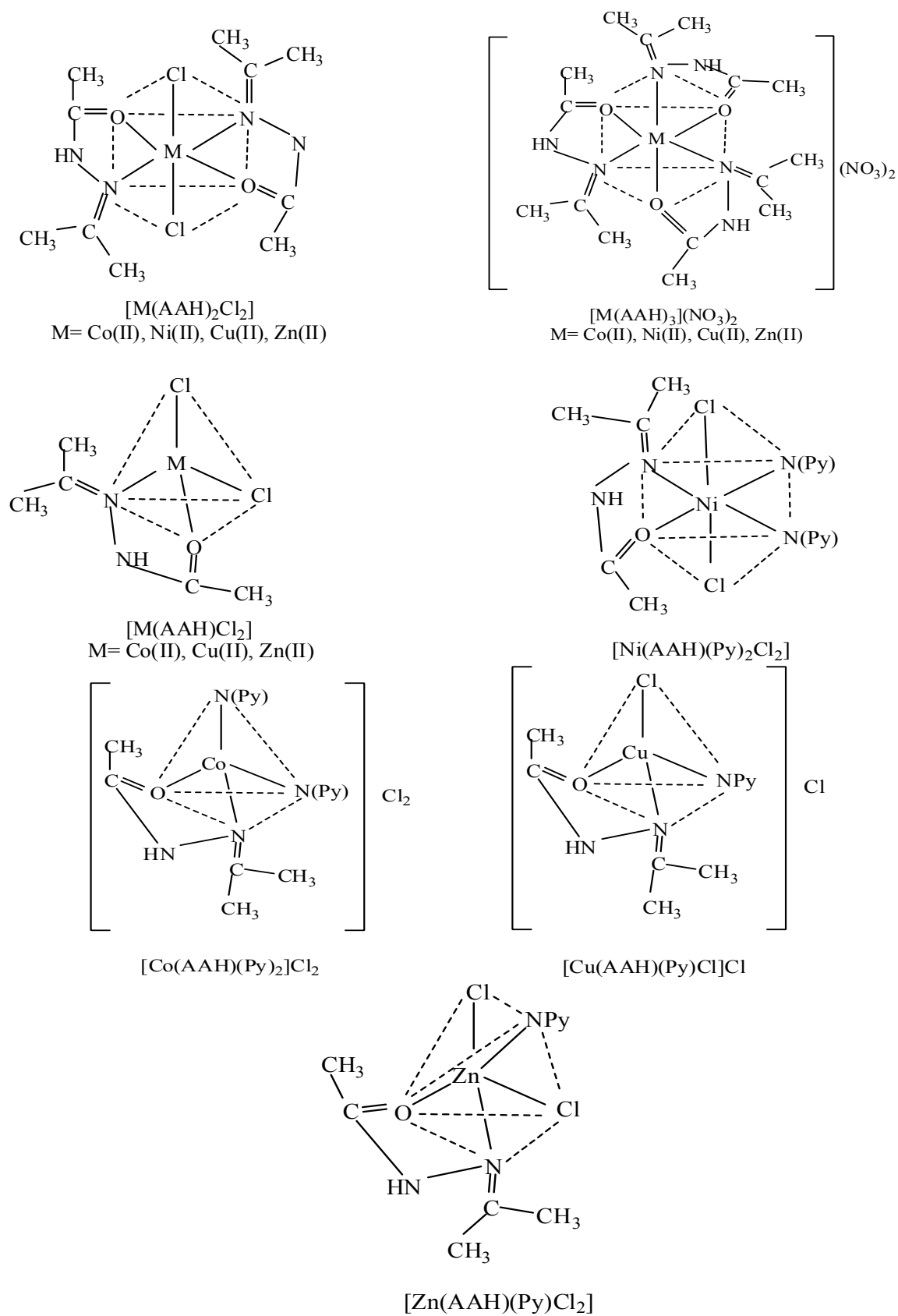
### CONCLUSION

The new aliphatic hydrazone acetone acetylhydrazone ligand and its complexes with Co(II), Ni(II), Cu(II) and Zn(II) were synthesized and characterized. Physicochemical studies allow to said that the ligand coordinated as neutral bidentate (ON) forming octahedral bis-complexes [M(AAH)<sub>2</sub>Cl<sub>2</sub>], tris-complexes [M(AAH)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> [M= Co(II), Ni(II), Cu(II), Zn(II)] Fig.(1) and the mixed ligand complex [Ni(AAH)(Py)<sub>2</sub>Cl<sub>2</sub>]. The mono complexes [M(AAH)Cl<sub>2</sub>][M= Co(II), Cu(II), Zn(II)] and the mixed ligand complexes [Co(AAH)(Py)<sub>2</sub>Cl<sub>2</sub>] and [Cu(AAH)(Py)Cl]Cl are expected to have tetrahedral geometry Fig. (1).

The free ligand and some of its complexes were evaluated in vitro as antimicrobial agents against Gram positive *Staph. aureus* and Gram negative bacteria *E. coli*.

The evaluated metal complexes have a moderate activity against Gram positive bacteria *Staph. aureus* and Gram negative *E. coli*, being Zn(II) complexes are the most active compound. It must be emphasized that the studied metal complexes were more active than the free ligand.



**Fig. 1: Proposed structures of the prepared complexes.**

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